Investigation of the ν_8 and ν_{21} bands of propane CH₃CH₂CH₃ at 11.5 and 10.9 μm : evidence of large amplitude tunnelling effects

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Investigation of the ν_8 band (B-type band, C-C symmetric stretch at 870.348 cm^{-1}), and ν_{21} band (A type band, CH_3 rock at 921.382 cm^{-1}) of propane (C_3H_8) using high resolution FTS spectra recorded at low temperature on the SOLEIL synchrotron source. The rotational energy levels in the upper states are split because of interactions with the internal rotations of the methyl groups, leading to the identification of AA, EE, AE and EA torsional components. An effective “vibration – torsion- rotation” Hamiltonian model and its associated line intensity code were built in G_{36} symmetry group.

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Investigation of the ν_8 and ν_{21} bands of propane $\text{CH}_3\text{CH}_2\text{CH}_3$ at 11.5 and 10.9 μm : evidence of large amplitude tunnelling effects.

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Abstract

We present the first investigation of the ν_8 band (C-C symmetric stretch at 870.348 cm^{-1}), together with an extended analysis of the neighbouring ν_{21} band (CH_3 rock at 921.382 cm^{-1}) of propane (C_3H_8). Our previous investigation of the ν_{21} A-type band [A.Perrin, F. Kwabia-Tchana, J.M.Flaud, L.Manceron, P.Groner, W.J.Lafferty. *J. Mol. Spectrosc.* **315**, 55 (2015)] revealed that the rotational energy levels of 21^1 are split because of interactions with the internal rotations of the methyl groups, leading to the identification of AA, EE, AE and EA torsional components. In this work, a similar behaviour was observed for the B-type ν_8 band and the analysis of the ν_{21} band was greatly extended. One of the results of the present study is to show that these torsional splittings are due to the existence of anharmonic and Coriolis resonances, coupling the 21^1 and 8^1 rotational levels to nearby highly excited levels of the two

internal rotations of the methyl groups. Accordingly, an effective “vibration – torsion-rotation” Hamiltonian model was built in the G_{36} symmetry group which accounts for both types of resonances. In parallel, a code computing the line intensities was developed to allow unambiguous torsional component assignments. The line assignments were performed using a high resolution (0.0015 cm^{-1}) infrared spectrum of propane, recorded with synchrotron radiation at the SOLEIL French light source facility coupled to a Bruker IFS-125 Fourier transform spectrometer. Finally, a linelist of positions and intensities which can be used for the detection of propane in the Earth and outer planets atmospheres was produced.

Keywords:

High resolution Infrared spectroscopy; Propane ($\text{CH}_3\text{CH}_2\text{CH}_3$); two equivalent methyl rotors; vibration- rotation resonances; large amplitude tunnelling;

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11 figures, 13 Tables

I Introduction

a) Atmospheric and planetary importance

Propane (C_3H_8) has been detected in the atmosphere of giant planets [1]. Also, in the Titan limb spectra recorded by the Cassini CIRS instrument, the presence of C_3H_8 was detected through several infrared bands like the ν_{26} (748cm^{-1}), ν_8 (869 cm^{-1}), ν_{21} (922cm^{-1}), ν_{20} (1053cm^{-1}) and ν_{25} (1192 cm^{-1}) bands [2]. At this occasion, it was noticed that the shape of the ν_{21} band in the cold atmosphere Titan spectrum appears somewhat different from the room temperature (PNNL spectrum) [3], due to the presence of hot bands on the short-wavelength side of the fundamental band in the laboratory spectrum.

In the Earth's atmosphere, propane (C_3H_8) is produced by biomass burning and is an indicator of pollution in urban areas [4]. The available high resolution spectroscopic data on propane are, however, rather sparse, and, as a consequence, only the ν_{26} and ν_{18} bands, located at 748 cm^{-1} and 1376 cm^{-1} respectively, have been used to retrieve propane abundances using line lists generated during previous high resolution detailed spectroscopic studies [5, 6].

b) Spectroscopic data

The main isotopologue ($^{12}\text{CH}_3^{12}\text{CH}_2^{12}\text{CH}_3$) of propane is an asymmetric top molecule with a C_{2v} symmetry equilibrium structure [7]. Among its 27 vibrational modes [8], the two lowest energy ones are associated to the two large amplitude methyl torsional modes located at $\sim 217(8)\text{ cm}^{-1}$ (ν_{14} , A_2 in the C_{2v} symmetry group) and $\sim 265(8)\text{ cm}^{-1}$ (ν_{27} , B_2), respectively [8,9], while the ν_9 band located at 369.22 cm^{-1} [10] corresponds to the low amplitude C-C-C (A_1) symmetric deformation. The barrier to internal rotation is estimated to be between 1139 and 1353 cm^{-1} depending on authors and methods [11, 12, 13]. Due to the presence of internal rotation, each rotational energy level is split into four components (AA, AE, EA and EE), with tunnelling splittings ranging from $\sim 10^{-4}\text{ cm}^{-1}$ to $\sim 2 \times 10^{-3}\text{ cm}^{-1}$ for the ground and the first two torsional excited states, ν_{14} and ν_{27} .

The rotational transitions within the vibrational ground state [7, 14-16] and the first two torsional excited states (ν_{14} and ν_{27}) [16] were measured using microwave and submillimeter techniques. In Ref. [16] the observed transition frequencies were satisfactorily reproduced using the SPFIT [17] and the ERHAM [18-22] theoretical approaches.

Cross sections of propane have been measured at low or medium resolution ([3, 23-26], and references therein) or at high resolution [26-28]. Also several Raman spectroscopy

investigations ([11, 12] and references therein) and ab initio calculations ([13] and references therein) have been performed.

As far as detailed line by line infrared investigations at high resolution are concerned, only a few bands among the 22 infrared active fundamental bands of propane have been analysed. This is because assigning the propane spectrum in the infrared region represents quite a challenge [5, 6, 10, 29, 30]. The spectra are indeed very dense because of the small values of the rotational constants ($A = 0.9742562313 \text{ cm}^{-1}$, $B = 0.2817271865 \text{ cm}^{-1}$ and $C = 0.2488055608 \text{ cm}^{-1}$) [16]. Moreover, lines belonging to hot bands contribute significantly, complicating the assignment process even at low temperatures.

During these first high resolution infrared investigations which involve, starting from the low frequency range, the ν_9 band located at 369.22 cm^{-1} [10] and the ν_{26} band at 748.531 [6, 29], only “classical” vibration rotation resonances were observed (without torsional splittings). This was also more or less the case for the ν_{19} , ν_{18} , ν_5 , ν_{17} , ν_{24} and ν_4 bands, located at 1338.965 , 1376.850 , 1461.072 , 1462.488 , 1471.875 and 1476.384 cm^{-1} respectively [5]. These bands involve indeed vibrational states with vibrational energies rather close to the torsional barrier heights. However, some series of transitions, belonging mainly to the ν_{18} band, appeared to be split into weak components [5]. The existence of these splittings (about 0.001 to 0.005 cm^{-1}) was explained by resonances coupling the 18^1 upper state energy levels with levels belonging to highly excited states involving the torsional modes ν_{14} and/or ν_{27} .

On the contrary, the overall set of transitions of the ν_{21} A-type band and of the ν_8 B-type band located at 921.384 cm^{-1} and 970.348 cm^{-1} respectively are split into torsional transitions. In addition, during the investigation of the ν_{21} band, some K_a series (mainly $K_a=6$ and 7) appeared to be perturbed by a dark state through a local C-type Coriolis resonance.

The main result of the present study is to explain the existence of these torsional components through the presence of anharmonic and Coriolis resonances coupling the 21^1 and 8^1 states with nearby highly excited torsional states involving ν_9 , ν_{14} and ν_{27} .

c) Torsional splitting in the (9^1 , 14^1 , 27^1) excited states of propane

The information can be derived from two sets of computations which combined ab initio calculations and/or low resolution Raman measurements or infrared data. The first one is a two-state computation involving the ν_{14} and ν_{27} torsional modes [11, 12]. The second one [13] is a three-state computation involving the ν_9 low amplitude mode together with ν_{14} and ν_{27} . The outputs of these studies are predicted lists for the AA, EE, EA, and AE

subcomponents band centres (E_{AA} , E_{EE} , E_{EA} and E_{AE}) for a set of ($v_9=0, v_{14}, v_{27}$) states covering the 0-1380 cm^{-1} energy range (Table 4 of Ref. [12]) and for a set of (v_9, v_{14}, v_{27}) states covering the 0-780 cm^{-1} energy range (Table 6 of Ref. [13]). In both calculations, the EA and AE torsional sub states have almost equal band centre values identified as $E_{AE\&EA}$:

$$E_{EA} \approx E_{AE} = E_{AE\&EA} \quad \text{Eq.(1)}$$

Also for a molecule with a high torsional barrier, the following well known relation links the AA, EE and EA and AE band centres [31, 32]:

$$(E_{EA\&AE} - E_{AA}) \approx 2 \times (E_{EE} - E_{AA}) = 2 \times \Delta_{EE,AA} \quad \text{Eq.(2)}$$

where

$$\Delta_{EE,AA} = (E_{EE} - E_{AA}) \quad \text{Eq. (3)}$$

It is interesting to compare the results of the two computations for the 0 to 780 cm^{-1} energy range. For E_{AA} , the values differ only by a few cm^{-1} (up to 3 cm^{-1}). However, for the $\Delta_{EE,AA}$ splittings, if the two computations agree on the (positive or negative) sign of $\Delta_{EE,AA}$, the absolute values quoted by Villa et al. [13] are about four times larger than those of Engeln et al. [12].

Therefore, when focussing on the 850-950 cm^{-1} energy range, the only information that one can extract from the computations are (i) a crude estimate of the AA band centres for the (v_9, v_{14}, v_{27})= $14^2 27^2$ and (v_9, v_{14}, v_{27})= $14^1 27^3$ dark vibrational states located around 872.8 and 929.1 cm^{-1} [13], respectively, (ii) the positive sign for the EE-AA torsional splittings ($\Delta_{EE,AA} = 0.79 \text{ cm}^{-1}$ and $\Delta_{EE,AA} = 0.44 \text{ cm}^{-1}$ for $14^2 27^2$ and $14^1 27^3$ respectively). We also need information for the (v_9, v_{14}, v_{27})= $9^1 27^2$ dark state which is presumed to be responsible for the existence of a C-type Coriolis resonance which perturbs the 21^1 energy levels for $K_a \approx 6$. Since the v_9 mode is not a torsional mode, we can assume that the $\Delta_{EE,AA}$ torsional splitting for (102) has a value analogous to what is computed for 27^2 ($\Delta_{EE,AA} \approx 0.005 \text{ cm}^{-1}$ and 0.02 cm^{-1} in Ref. [12] and [13] respectively). This value is significantly smaller than for $14^2 27^2$ and $14^1 27^3$. Therefore, the torsional splitting in the $9^1 27^2$ dark state was not accounted for during this study.

The paper is organised in the following way. First, the experimental spectrum used during this investigation is described. Then, the symmetry properties are discussed. The

descriptions of the Hamiltonian and of the line intensity codes are then given. Finally the results of the assignments performed for the ν_8 band and ν_{21} bands are presented and discussed.

II Experimental details and wavenumbers calibration

a) Experimental details

The high-resolution absorption spectrum of propane (810-970 cm^{-1} spectral range) was recorded using the AILES Beamline at SOLEIL, coupled to a Bruker IFS125HR Fourier transform spectrometer [33, 34] and the SOLEIL-LISA cryogenic cell [35]. The instrument was equipped with a KBr/Ge beamsplitter. The synchrotron source was operated with a 430 mA ring current and a liquid nitrogen-cooled HgCdTe (MCT) detector was used in conjunction with a 500-1300 cm^{-1} band pass optical filter to improve the S/N ratio. The spectrometer was evacuated to about 5×10^{-3} Pa in order to minimize H_2O and CO_2 absorptions. The spectrum was recorded with a nominal resolution of 0.0015 cm^{-1} . The temperature was regulated to 142 ± 2 K along the entire optical path, set to 45.14 m. Propane was purchased from Sigma Aldrich and used without further purification. The chemical purity of propane was specified as 99.97%. The following procedure was used for measurements: first a background spectrum was recorded at the same temperature of 142 K while the cell was continuously evacuated; next the infrared gas cell was filled with 14.0 (3) Pa of pure propane. The sample pressure in the cell was measured using a home-made cryogenic precision capacitive pressure gauge [36].

b) Wavenumbers calibration

The spectrum was calibrated with residual CO_2 lines observed in the spectrum with their wavenumbers taken from HITRAN [37]. The quantity $\epsilon = ((\nu_{3716}/\nu_{\text{this work}}) - 1)$ has been calculated using about 30 transitions between 650–680 cm^{-1} (CO_2). The mean value $\langle \epsilon \rangle = -8.48 \times 10^{-7}$ has been found and the resulting precision is ± 0.000063 cm^{-1} (RMS) for well isolated lines. We then estimated the absolute accuracy of the measured propane line positions as the square root of the sum of squares of the accuracy of the line positions of CO_2 from [37] (better than 0.0001 cm^{-1}) and two times the RMS of the wavenumber calibration, yielding 0.0002

cm⁻¹. Figure 1 gives an overview of the experimental spectrum together with the modelling of the B-type ν_8 and A-type ν_{21} bands.

III Theoretical considerations

The overall structure of propane [7] is presented on Fig. 2. Since torsional tunneling has to be considered, the G_{36} inversion permutation group [38] which is quoted in Table 1, has to be used instead of the C_{2v} point group, which is suitable only for a rigid molecule [5]. The tables giving the reverse correlation between G_{36} and the C_{2v} point group can be found in Refs. [30, 39]. Table 2 lists the symmetry types of the 27 vibrational states of propane together with those of the rotational energy levels $|Rot\rangle = [J, K_a, K_c]$. This table gives also in the I' representation ($z=A, x=B, y=C$) the symmetry type of the E^+ , O^+ , E^- and O^- ($|J, K|$ even or odd, $\gamma=\pm 1$) symmetrized Wang's type base functions, which, are:

$$\text{for } K \neq 0 \quad |JK\gamma\rangle = \frac{1}{\sqrt{2}} (|JK\rangle + \gamma |J-K\rangle) \quad \text{with } \gamma = \pm 1 \quad \text{Eq.(4,a)}$$

$$\text{and } |JK = 0, \gamma = +1\rangle = |JK = 0\rangle \quad \text{for } K=0. \quad \text{Eq.(4,b)}$$

It can be seen that only the first four (A_1 to A_4) representations of the G_{36} group are to be used for the classification of any rotational wave function $[J, K_a, K_c]$ or of any $|v_1, \dots, v_{27}\rangle$ vibrational state of propane.

For propane, the α_1 and α_2 angles (with α_1 and $\alpha_2 \in [-\pi, \pi]$) [12] describe the torsions of the CH_3 - groups about C-C bonds with the convention that these angles are taken to be zero if the predetermined hydrogen of the top lies in C-C-C plane. The AA, AE, EA and EE torsional wave functions are expansions of tensorial products of the $\Psi_{3n_1+\sigma_1}(\alpha_1) \otimes \Psi_{3n_2+\sigma_2}(\alpha_2)$ torsional basis wavefunctions, with:

$$\Psi_{3n_k+\sigma_k}(\alpha_k) = \frac{1}{\sqrt{2\pi}} \exp[i(3n_k\alpha_k + \sigma_k)], \quad \text{with } k=1,2 \quad \text{Eq.(5)}$$

In this expression, σ_1 and σ_2 are the torsional phase factors, modulo 3, which can take the values $\sigma=0, -1, +1$. The AA, AE, EA and EE subcomponents are associated to the $(\sigma_1, \sigma_2) = (0,0), \{(1,-1), (-1,1)\}, \{(1,1), (-1,-1)\}$ and $\{(1,0), (0,1), (-1,0), (0,-1)\}$ phase factors, respectively.

Table 2 gives the symmetry types of the four torsional wavefunctions ($|Tors_0\rangle = AA, AE, EA$ and EE) in the ground vibrational state $|V=0\rangle$. Using Tables 1 and 2 it is easy to

deduce the symmetry character of the $|V;Tors\rangle$ “vibration- torsion” wavefunctions. This symmetry character is indeed the product of the Γ symmetry species of the vibration and of the ground state torsional components :

$$\Gamma|V;Tors\rangle = \Gamma|V\rangle \otimes \Gamma|Tors_0\rangle \quad \text{Eq.(6)}$$

In the same way it is easy to define the symmetry species in G_{36} of any $|V;Tors; Rot\rangle$ “vibration torsional rotation” wavefunction, according to the vibrational quanta in $|V\rangle$, the $|Tors\rangle = AA, AE, EA$ or EE torsional wavefunction and the K_a and K_c parity. For example, Table 3 gives the Γ symmetry species for the $|V=0;Tors; J K_a K_c\rangle$ torsion- rotation wavefunctions in the ground ($v=0$) vibrational state. For an AA component, only one single parity set is associated to each $\Gamma = A_1$ to A_4 symmetry. For the EA (resp. AE) component, two parity sets are present for $\Gamma = E_1$ to E_2 (Resp. $\Gamma = E_3$ to E_4). Finally, for an EE component, the four parity sets are associated to $\Gamma = G$. Table 3 gives also the nuclear spin statistical weights ($g_{Nuclear}$) associated to the torsion- rotation levels in the ground vibrational state of propane.

IV Assignment process

a) The ground state energy levels

The effects of the torsional motion in the ground state have negligible impact in the infrared region; so, in the present work, the ground state energy levels were computed using the ground state parameters of Drouin et al. [16] using an A-type Watson Hamiltonian in the I' representation [40]. For medium and high K_a values, the $[J, K_a, J-K_a]$ and $[J, K_a, J-K_a+1]$ levels become “degenerate” due to the particular values of the rotational constants ($A \sim 0.97426 \text{ cm}^{-1}$, $B \sim 0.28173 \text{ cm}^{-1}$, and $C \sim 0.24881 \text{ cm}^{-1}$). In the rest of this paper, the notation “ $K_c=d$ ” and “ $K_c \neq d$ ” stands for “degenerate” $[J, K_a, K_c]$ levels (with $K_c=J-K_a$ and $K_c=J-K_a+1$), and “non-degenerate” levels respectively.

As will be seen later, the observed torsional structure changes dramatically depending on the existence or non-existence of a K_c degeneracy for the rotational transitions involved in the cluster. Therefore, at the starting point of the present analysis, it was necessary to guess – approximatively – the form of the observable torsional clusters and the possible occurrence of a K_c degeneracy. To do so we used the computed ground state energy levels [16] and defined the following separation limit:

$$\delta = |E([J, K_a, K_c=J-K_a]) - E([J, K_a, K_c=J-K_a+1])| \quad \text{Eq.(7.a)}$$

$$\delta \leq \delta_{\text{limit}} \text{ for } "K_c=d", \quad \delta > \delta_{\text{limit}} "K_c \neq d" \quad \text{Eq.(7.b)}$$

$$\text{with } \delta_{\text{limit}} \approx 0.001 \text{ cm}^{-1} \quad \text{Eq.(7.c)}$$

Indeed, for ν_8 (resp. ν_{21}) transitions involving ground state energy levels with $\delta \leq \delta_{\text{limit}}$, the effects of an A-type Coriolis resonance within the 8^1 (resp. 21^1) upper level are quite significant for EE and AE torsional subcomponents, affecting strongly the form of the cluster. In such conditions, Fig. 3 gives the $K_c=d$ threshold limit for the ground vibrational state energy levels, according to K_a and J values. This figure is restricted to the range of K_a and J values ($K_a \leq 18$ and $J \leq 50$) which could be reached during the assignment process. All the $[J, K_a=1, K_c]$ ground state levels are “non-degenerate”, while for $K_a \geq 10$ all $[J, K_a, K_c=d]$ levels are “degenerate” K_c levels.

b) The ν_8 and ν_{21} bands : structure of the torsion – rotation transitions

According to symmetry considerations in the C_{2v} point group, the ν_8 and ν_{21} bands are B- and A-type bands with $(|\Delta K_a| = \text{odd}, |\Delta K_c| = \text{odd})$ and $(|\Delta K_a| = \text{even}, |\Delta K_c| = \text{odd})$ selection rules, respectively. However, this is true only in the C_{2v} point group approach and for the AA subcomponents. Additional transitions are indeed symmetry- allowed for the other torsional components.

The assignment process proved to be difficult for both the ν_8 and ν_{21} bands because we are dealing with a very dense and highly perturbed spectrum. In addition, each infrared vibration-rotation transition is split into several torsional subcomponents. Then, since the ground state combination differences cannot fully help in the identification of the torsional labels, we had to rely on the intensity pattern of the sub-components. The intensities of the torsional patterns depend indeed on the associated vibration rotation transitions.

Normally, each vibration-rotation transition of ν_8 and ν_{21} should appear split into three subcomponents AA, EE, (EA and AE), because the EA and AE torsional sub states have almost equal band centers (see Eqs. 1-3). However, except for the AA subcomponents, a Coriolis resonance within the $\nu_8=1$ or $\nu_{21}=1$ excited state may significantly affect the torsional structure. In principle, A-type, B-type, or C-type Coriolis resonances are symmetry allowed in the (EE and AE), (EE and EA), or EE subcomponents, respectively. Among these the possibilities quoted above, the A-type Coriolis resonance leads to the most significant effects

for K_c “degenerate” sublevels by splitting apart the $[J K_a K_c=J-K_a]$ and $[J K_a K_c=J-K_a+1]$ levels for the EE or AE torsional substates. The consequence is that the structure of the torsional clusters in the observed spectrum looks quite differently from the expected pattern, depending on the existence (or non- existence) of a K_c degeneracy.

- (Low K_a values): For series involving “non degenerate” K_c values, triplets of lines are generally observed, with a central line about twice as strong as the two other ones. Using the predictions of Table 4 which states that the relative intensities are in the ratio $AA/EE/(AE+EA)= 36/64/36$ or $AA/EE/(AE+EA)= 28/64/28$ for even or odd values of $(K_a'' + K_c'')$, respectively, it is easy to deduce that the central line is the EE torsional component, while the other two, of equal intensities, are the AA and the (AE+EA) components. Examples of this type of triplet patterns are observable on the left hand side of Figure 4.

- (High K_a values): For series involving “degenerate” K_c values the K_c degeneracy is lifted for the EE and AE subcomponents, but not for the AA and EA subcomponents. This is why six lines are then observed with a $64/64/64/32/16/16$ intensity ratio. The two weakest components (relative intensity ≈ 16) are the “non-degenerate” ($K_c=J-K_a$) and ($K_c=J-K_a+1$) AE transitions, while the EA “degenerate” ($K_c'=d$) component is twice as strong (relative intensity ≈ 32). Finally, the three strongest lines, with similar intensities (intensity ratio $64/64/64$) correspond to the ($K_c'=d$) AA “degenerate” pair, together with the two split ($K_c'=J'-K_a'$) and ($K_c'=J'-K_a'+1$) EE transitions. For such subcomponents, the torsional assignment (one AA, and two EE) was a tedious task, because no information can be provided by the intensity pattern. Figure 5 and the high frequency range of Figure 4 provide good examples of the “high K_a ” torsional structure.

- (Intermediate K_a values) For J and K_a values corresponding to border cases between “degenerate” and “non-degenerate” K_c values, the cluster system is even more complex, and this is evidenced on Figures 6 and 7. Indeed, C_{2v} non-allowed transitions (with $(|\Delta K_a| = \text{even}; |\Delta K_c| = \text{even})$ for ν_{21} and $(|\Delta K_a| = \text{odd}; |\Delta K_c| = \text{even})$ for ν_8 are also observable for EE and AE in addition to the classical A and B-type transitions, respectively.

In conclusion, one can say that setting unambiguously a torsional assignment to a given $[J' K_a' K_c']-[J K_a K_c]$ torsional subcomponent was not an easy task.

Once a few lines were firmly assigned, an initial fit was performed yielding preliminary values for the band centers and rotational and torsional constants and interacting parameters for the 21^1 and 8^1 vibrational states. These preliminary constants enabled the computation of a synthetic spectrum of line positions and relative intensities, which was then used to perform new assignments leading to an improvement of the upper state parameters. This process was pursued until it was not possible to perform additional assignments. The final results are given in Table 5 for the ν_{21} and ν_8 bands.

V Hamiltonian matrix

a) Introduction

Owing to the complexity of the vibration rotation resonances observed during the present analysis, it proved inadequate to use the codes which were developed in the microwave literature [18-22, 41-43].

During our previous investigation of the ν_{21} band [30] we used a rather “primitive” theoretical approach which consists in building up three different Watson-type Hamiltonians, each of them being associated to a given set of AA, EE or EA-AE torsional energy levels. Clearly, this approach is not satisfactory, because it cannot account for the two types of clustering of the torsion- rotation energy levels and leads to erroneous torsional assignments. Furthermore, the C-type Coriolis resonance, which perturbs several rotational series of the ν_{21} band, was not considered at that time. Therefore we use here a different approach in which a single “vibration – torsion- rotation” effective Hamiltonian is used for the whole set of vibration-rotation-torsion energy levels. Using such an effective approach is justified because information concerning the high excited torsional states of propane is sparse and inaccurate. Therefore, it was decided to build a Hamiltonian matrix which is issued from our experience on C_{2v} molecules and is adapted to the G_{36} symmetry group. This means that the model is able to account for any local anharmonic or Coriolis resonance and takes into consideration the torsional structure by adding to each rotational operator a periodic expansion which accounts for the (σ_1, σ_2) torsional quantum number of the considered torsional substate.

b) General form of the Hamiltonian matrices

The general form of the Hamiltonian matrices used for the $\{8^1, 14^2 27^2\}$ and $\{21^1, 14^1 27^3, 9^1 27^2\}$ interacting states is given in Table 6. Table 7 gives the different type of rotational

operators (Watson-type, anharmonic or Coriolis type) which, according to symmetry considerations, may be considered in the v - diagonal as well as in the $v' \leftrightarrow v$ off diagonal blocks, depending on the considered torsional submatrix (AA, EE, AE et EA).

Table 8 details the expansion of the Watson type operators (written in the I' representation and in the A-type reduction), and of the anharmonic, A-type, B-type and C-type Coriolis operators.

c) *Fourier transform expansion of the parameters*

In order to account for the torsional motion, we perform, in Table 9, a Fourier expansion of the parameters involved in the Hamiltonian matrix. The $S_q^{\sigma_1, \sigma_2}(K_{\text{avg}})$ expressions quoted in Table 9,b represent the torsional contribution to the matrix element of the effective Hamiltonian operators. These expressions are sinusoidal expansions in $\chi = \pi \rho K_{\text{avg}} / 3$ terms, where $K_{\text{avg}} = (K + K')/2$ is the average value of the K and K' values of the two Wang-type basis functions involved in the considered matrix element and ρ is the internal rotation parameter.

Our approach is rather similar to the one adopted by Drouin et al [16] since our ρ parameter in Table 9 is in fact “ ρ_a ”, the A- axis component of ρ . The present formalism is less sophisticated than the dual rotor effective Hamiltonian model (ERHAM) developed by P.Groner [18-22], which involves Wigner’s type $d_{KK'}^{(J)}(\beta)$ matrices together with sinusoidal terms in $\chi = \pi \rho K_{\text{avg}} / 3$ in the expansion of the parameters. However, the ERHAM model which was successfully used during the investigation of acetone [20-21] and dimethyl ether [19], cannot account for vibration rotation resonances, which are one of the major problems that we had to face to during this study.

As compared to its “torsion free” E_v^0 counterpart, the vibrational energies of the AA, EE, EA, or AE torsional substates of a given v vibrational state are:

$$\text{AA} : E_v^{\sigma, \sigma_2=0,0} = E_v^0 + 0 + \text{Tor}_1^v + \text{Tor}_2^v + \text{Tor}_3^v + \text{Tor}_4^v$$

$$\text{EE} : E_v^{\sigma, \sigma_2=1,0} = E_v^0 + \text{Tor}_0^v + \text{Tor}_1^v / 4 + \text{Tor}_2^v / 4 + \text{Tor}_3^v + \text{Tor}_4^v / 2$$

$$\text{EA} : E_{\nu}^{\sigma, \sigma_2=1,1} = E_{\nu}^0 + 2 \times \text{Tor}_0^{\nu} - \text{Tor}_1^{\nu} / 2 - \text{Tor}_2^{\nu} / 2 + \text{Tor}_3^{\nu} + \text{Tor}_4^{\nu}$$

$$\text{AE} : E_{\nu}^{\sigma, \sigma_2=1,-1} = E_{\nu}^0 + 2 \times \text{Tor}_0^{\nu} - \text{Tor}_1^{\nu} / 2 - \text{Tor}_2^{\nu} / 2 + \text{Tor}_3^{\nu} - \text{Tor}_4^{\nu} / 2 \quad \text{Eqs (8)}$$

With these definitions of Tors_q^{ν} , the ν_8 and ν_{21} least squares fit calculations lead for $q > 0$ to $\text{Tors}_{q \neq 0}^{\nu}$ values for the $\nu=14^2 27^2$ or $\nu=14^1 27^3$ dark states which are significantly smaller (in absolute value) than their associated $q=0$ Tors_0^{ν} corresponding values. Therefore the AA-vibrational energy, $E_{\nu}^{\sigma, \sigma_2=0,0}$, is almost equal to E_{ν}^0 , and Eqs. (1) and (2) are fulfilled.

VI Results of the energy level calculations

The experimental vibrational - torsional – rotational energy levels were introduced into two least squares fit calculations to derive a set of $\{8^1, 14^2 27^2\}$ and $\{21^1, 14^1 27^3, 9^1 27^2\}$ vibrational energies, torsional, rotational and anharmonic or Coriolis type interacting parameters. These parameters are quoted, together with their associated uncertainties, in Table 10 and 11 for the 8^1 and 21^1 computations, respectively. During these computations we tried to adjust the ρ internal rotation parameter. However it proved that the ρ term is highly correlated with the Tors_0^{ν} torsional shifts ($\nu=14^2 27^2$ or $\nu=14^1 27^3$). Therefore it was decided to maintain ρ at the value determined by Drouin et al. [16]:

$$\rho = 0.1511 \quad \text{Eq.(9)}$$

Let us notice that, because of the complexity of the vibration–rotation resonances and because of possible errors in the torsional labelling, the parameters gathered in Tables 10 and 11 are only effective. For example the values obtained for the A rotational constants are rather large ($0.993 \leq A \leq 1.14 \text{ cm}^{-1}$ as compared to the ground state value $A^0 = 0.9742562313 \text{ cm}^{-1}$ [16]). The values of some centrifugal distortion constants (mainly Δ_K) are also quite large.

Nevertheless, the values obtained for the band centers of the $14^2 27^2$ and $14^1 27^3$ dark states $\nu_{14142727} = 872.5168(1)$ and $\nu_{14272727} = 932.8751(2) \text{ cm}^{-1}$ differ little from the predictions given in Ref. [12] ($^{\text{Pred}}\nu_{14142727} = 872.8$ and $^{\text{Pred}}\nu_{14272727} = 929.1 \text{ cm}^{-1}$).

The statistical analysis on the results of the energy levels calculations are presented in Table 5. It is clear that it was not possible to reproduce the energy levels to within experimental accuracy.

Several reasons can be invoked:

- A very poor knowledge of the torsional structure for the states involving high ν_{14} or ν_{27} vibrational quanta. This is why the local resonances involving the $14^2 27^2$ and $14^1 27^3$ dark vibrational states are so difficult to identify and reproduce correctly.
- The imperfect quality of the model used to account for the resonances and for the torsional structure.
- Possible incorrect torsional or rotational assignments during the analysis process.

VII Line intensity calculations

The intensity of a line is given (in $\text{cm}^{-1}/(\text{molecule} \cdot \text{cm}^{-2})$) by [44]:

$$k_{\tilde{\nu}}^N = \frac{8\pi^3 \tilde{\nu}}{4\pi\epsilon_0 3hc Z(T)} g_{\text{nucl}} \left(1 - \exp\left(-\frac{hc\tilde{\nu}}{kT}\right) \right) \exp\left(-\frac{hcE_A}{kT}\right) R_A^B \quad \text{Eq.(10)}$$

where A and B are the lower and upper levels of the transition, respectively, $\tilde{\nu} = (E_B - E_A)/hc$ is the wavenumber of the transition, g_{nucl} are the nuclear spin factors, given in Table 3 according to the 9 symmetry species in G_{36} , and $Z(T)$ is the total partition function at the temperature T.

Several computations of $Z(T)$ were performed for propane in the literature [16, 26, 45]. As a final result, these authors provide an empirical polynomial expansion of $Z(T)$ as a function of the temperature:

$$Z(T) = \sum_{i=0,4} a_i \times T^i \quad \text{Eq.(11)}$$

One can notice that the $Z(T)$ values proposed by Drouin et al. [16] or Sung et al. [26] and Fischer and Gamache [45] differ significantly, not only in their absolute values, but also in their temperature dependences. For the present study, we cannot use any of these expressions of $Z(T)$ [26, 45]. Indeed, both computations were performed using incorrect values of the g_{nucl} nuclear spin factors (a constant value $g_{\text{nucl}}=1028$ for all levels, and the acetone nuclear spin weights, in Ref. [45] and in Refs. [16, 26], respectively).

As usual for molecules with low amplitude modes [46], performing a precise computation of $Z(T)$ requires a good knowledge of the rotational, vibrational and torsional spectroscopic parameters, and this is clearly not the case for propane. In Refs. [16,26] the computation of $Z(T)$ accounts for the fact that the rotational constants in the 14^1 and 27^1 states differ from those of the ground state. However, in order to get accurate $Z(T)$ values, other sources of errors should be considered, like the rather unprecise knowledge of the fundamental torsional modes (ν_{14} and ν_{27}), and of the overtones states involving ν_9 , ν_{14} , and ν_{27} (see for example Table 4 of Ref. [12] and Table 6 of Ref. [13]).

Knowing these limits, we decided to compute $Z(T)$ in the harmonic approximation. More explicitly $Z(T)$ was written as the product of its vibrational and rotational contribution.

$$Z(T) = Z_{\text{vib}}(T) Z_{\text{rot}}(T) \quad \text{Eq.(12)}$$

The vibrational part $Z_{\text{vib}}(T)$ was computed in the harmonic oscillator approximation using the vibrational frequencies quoted in Ref. [8] or, when existing, derived from high resolution investigations [5, 10, 6, 30, this work]. For the calculation of the rotational part $Z_{\text{rot}}(T)$, we used the ground state rotational constant of Ref. [16], together with the g_{nucl} values of Table 3. The results of the present computations performed up to $J=99$ are presented in Table 12 for various temperatures. The T - polynomial dependence of $Z(T)$ in the $70 \text{ K} \leq T \leq 320 \text{ K}$ temperature range from these calculations is:

$$Z(T) = 7.41945 \times 10^6 - 1.67279 \times 10^5 \times T - 1.33661 \times 10^3 \times T^2 - 4.17648 \times T^3 + 0.00527 \times T^4 \quad \text{Eq.(13)}$$

The last term of Eq.(8), R_A^B , is the square of the matrix element of the transformed transition moment operator μ_Z' :

$$R_A^B = \left| \left\langle v', J' K_a' K_c' \left| \mu_Z' \right| 0, J'' K_a'' K_c'' \right\rangle \right|^2 \quad \text{Eq.(14)}$$

In this expression, μ_Z' is the Z - component of the transformed dipole moment operator [44], which can be expanded as usual as:

$$\mu_Z' = \sum_{v' \in B'} |0\rangle \nu \mu_Z' \langle v'| \quad \text{Eq.(15)}$$

where v' belongs to the upper $B' = \{8^1, 14^2 27^2\}$ (resp. $B' = \{21^1, 14^1 27^3, 9^1 27^2\}$) vibrational polyads of interacting states and where $|v=0\rangle$ stands for the ground state.

The upper and ground state rovibrational wavefunctions are expanded as:

$$\begin{aligned} |v', J' K'_a K'_c\rangle &= \sum_{v' \in B'} \sum_{K', \gamma'} C_{v'}^{\gamma' K'} |v'\rangle |J' K' \gamma'\rangle \\ |v=0, J K_a K_c\rangle &= \sum_{K''} C_0^{\gamma'' K''} |J K'' \gamma''\rangle \end{aligned} \quad \text{Eqs.(16)}$$

In Eqs.(16) the $C_{v'}^{\gamma' K'}$ coefficients are obtained from the diagonalization of the Hamiltonian matrices (Tables 6).

In the C_{2v} approach, only B-type or A-type transitions are to be observed for the v_8 or v_{21} band, respectively. Although this is formally exact only for the AA subcomponents, the transition moment operator was written as:

$$v''=0 v' \mu_Z' = \sum_j {}^0 v' \mu_j^X A_j^X, \quad \text{Eq.(17)}$$

Where X stands for B or A for the v_8 or v_{21} band, respectively, and the expansions of the A_j^X rotational operators are quoted in Ref. [44]. In our case the expansions were restricted to the main terms, namely:

$${}^0 8 \mu_Z' = {}^0 8 \mu_1^B \varphi_x \text{ and } {}^0 21 \mu_Z' = {}^0 21 \mu_1^A \varphi_z \quad \text{Eq.(18)}$$

Where φ_α is the direction cosine between the Z-laboratory fixed axis and the α molecular axis and where the ${}^v v' \mu_j^X$ constants are the transition moment parameters.

Since the spectrum used for the present investigation was not optimized for measuring precisely intensities, we had to scale the intensities, we had to scale the ${}^0 8 \mu_1^B$ and ${}^0 21 \mu_1^A$ constants using band intensity values measured in the literature. They are (in $10^{-19} \text{ cm}^{-1}/(\text{cm}^{-2} \cdot \text{molecule})$ units) at 296K¹ :

$$S_{11\mu\text{m}}(296\text{K}) = 2.82 \pm 0.017 [26],$$

$$S_{11\mu\text{m}}(296\text{K}) = 2.98 \pm 0.069 [3],$$

¹ Let us emphasize that we did not account for the 296K measurements in Ref. [28] which are scaled on the PNNL values [3]

$$S_{11\mu\text{m}}(296\text{K}) = 3.28 \pm 0.07 [25],$$

$$\text{and } S_{11\mu\text{m}}(296\text{K}) = 2.81 \pm 0.55 [24]. \quad \text{Eqs. (19)}$$

In the present work, we used for $S_{11\mu\text{m}}(296\text{K})$ a weighted mean value deduced from these rather consistent measurements:

$$S_{11\mu\text{m}}(296\text{K}) = 2.853 \pm 0.107 \times 10^{-19} \text{ cm}^{-1}/(\text{cm}^{-2} \cdot \text{molecule}) \text{ at } 296\text{K} \quad \text{Eq.(20)}$$

In Eqs. (19) and (20), $S_{11\mu\text{m}}(296\text{K})$ is the total band intensity at 11 μm , which includes the contribution of hot bands. Using the method described in Ref. [47] it is possible to estimate the intensity of the associated (ν_8 and ν_{21}) cold bands associated to the 11 μm region by using the expression:

$$S_{11\mu\text{m}}(T) \approx Z_{\text{vib}}(T) \times (S_{\nu_8}^*(T) + S_{\nu_{21}}^*(T)) \quad \text{Eq.(21)}$$

In this equation, $Z_{\text{vib}}(T)$ is the vibrational partition function at the temperature T (see Table 12), while $S_{\nu_8}^*(T)$ and $S_{\nu_{21}}^*(T)$ are the intensities of the cold ν_8 and ν_{21} bands, together with their associated resonating dark bands ($2\nu_{14}+2\nu_{27}$; $\nu_9+2\nu_{27}$ and $\nu_{14}+3\nu_{27}$ for ν_8 and ν_{21} , respectively).

The other information which is of importance is the intensity ratio of the ν_{21} and ν_8 bands. Since a minimum of the infrared signature is observed around 892 cm^{-1} in the propane cross sections, it is possible to consider that below (resp. above) this 892 cm^{-1} limit, ν_8 and its associated hot bands (resp. ν_{21} and its associated hot bands) provide the bulk of the contribution to the observed infrared signature. This is confirmed by our high resolution simulation (see Fig. 1). Also Giver et al. [25] provide separately band intensity values in the $817\text{-}892$ and $892\text{-}1000 \text{ cm}^{-1}$ spectral ranges. Using the various literature data, we estimate the intensity ratio of the cross sections above and below 892 cm^{-1} . One gets:

$$R_{\text{low}}^{\text{high}}(296\text{K}) = (S_{\sigma > 892 \text{ cm}^{-1}}(296\text{K}) / S_{\sigma < 892 \text{ cm}^{-1}}(296\text{K}))$$

$$\begin{aligned}
 R_{\text{low}}^{\text{high}}(296\text{K}) &\approx 2.10 [25]; \\
 R_{\text{low}}^{\text{high}}(296\text{K}) &\approx 2.011 [3]; \\
 R_{\text{low}}^{\text{high}}(296\text{K}) &\approx 2.336 [26]; \\
 R_{\text{low}}^{\text{high}}(296\text{K}) &\approx 2.214 \text{ at } 296\text{K} [28]
 \end{aligned}
 \tag{Eq.(22)}$$

Averaging these values, one gets:

$$R_{\text{low}}^{\text{high}}(T = 296\text{K}) = 2.15 \pm 0.12 \tag{Eq.(23)}$$

Using all the information described previously, we can then determine the ν_8 and ν_{21} line intensity parameters. For this, we calculated synthetic spectra and summed the ν_8 and ν_{21} line intensities in the 817-892 and 892-1000 cm^{-1} spectral ranges. The ${}^08\mu_1^{\text{'B}}$ and ${}^021\mu_1^{\text{'A}}$ constants were determined so that Eqs. (20), (21), and (23) are fulfilled.

The final values that we obtained for the ${}^08\mu_1^{\text{'B}}$ and ${}^021\mu_1^{\text{'A}}$ transition moments are:

$${}^08\mu_1^{\text{'B}} \approx 1.753 \times 10^{-2} \text{ Debye} \text{ and } {}^021\mu_1^{\text{'A}} \approx 2.175 \times 10^{-2} \text{ Debye}^2 \tag{Eq.(24)}$$

Let us notice that, for both parameters, only the absolute value can be obtained.

VIII Synthetic spectrum and validations:

(a) Line intensity calculations:

Using the vibrational energies and the rotational, torsional and coupling constants given in Tables 10 and 11 for the upper interacting states, and in Ref.[16] for the ground state, together with the ${}^08\mu_1^{\text{'B}}$ and ${}^021\mu_1^{\text{'A}}$ transition moment constants given Eqs.(24) we have generated at 142 K and 296K comprehensive lists of line positions and intensities for the ν_8 and ν_{21} bands of propane.³

As the energy level calculation was not fully satisfactory, the calculated upper state energy levels were replaced by the experimental ones whenever possible. The calculations were performed for a "pure" isotopic sample of propane using an intensity cutoff of $1 \times 10^{-25} \text{ cm}^{-1}$

² (1 Debye= $3.33564 \times 10^{-30} \text{ C} \times \text{m}$)

³ These linelists can be obtained upon request from the authors.

¹/(molecule.cm⁻²). The results of these calculations (maximum values of J and K_a, frequency ranges, band intensity details etc..) are collected in Table 13. Let us notice that, because of local resonances, the predicted linelists include weak lines involving the dark resonating states

(b) *Validation with the observed high resolution FTS spectrum*

Figure 1 presents an overview of the comparison between the observed spectrum and the calculation for the ν_8 and ν_{21} bands. Also figures 4 to 10 give detailed views of various portions of the spectrum.

Figures 4 and 5 present portions of the R branch of the ν_{21} band around 931.3 cm⁻¹ and 927.88 cm⁻¹, respectively. On the left hand side of Figure 4, the triplet patterns (AA/ EE/ AE&EA) are characteristic of lines involving low K_a values.

The right hand sides of Figures 4 and 5 present the structures which are observed for transitions involving high K_a values. In this case, six torsional subcomponents are observable, and their relative intensities are given in Table 4. The torsional identification of the weakest lines (EA for the medium one, and AE for the two weakest ones) was unambiguous. Note that the two AE subcomponents involve the same E₁ or E₂ submatrix for the upper levels. For the three strongest components, with equal intensities, only the calculations can provide the correct torsional assignment, since two of them are split into K_c=J-K_a and K_c=J-K_a+1 EE transitions, while the third one is the EA “degenerate” (K'_c=d) transition.

Figures 6 and 7 give a portion of the R branch of the ν_8 band at 881.0 cm⁻¹ and of the P branch of the ν_{21} band at 915.6 cm⁻¹. In these spectral regions the transitions involve “intermediate” K_a values (see Figure 3 and Table 4). Therefore, for the EE subcomponents, C-type transitions for the ν_8 band, (resp. “forbidden” transitions with ΔK_a =even, ΔK_c =even for the ν_{21} band) are clearly observable in the spectrum, together with the “classical” B-type (resp. A-type) lines

Figure 8 gives a portion of the P branch of the ν_{21} band at 915.06 cm⁻¹. The transitions involve low K_a values. A classical “triplet” structure in (AA/ EE/ AE&EA) is observed for [11 2 10]-[12 2 11], with equal intensities for the AA and the (EA&AE) cluster. For the [11 3 9]-[12 3 10] transition, the AA and EE components behave normally, while the AE and EA torsional components do not coincide because a local resonance is affecting the EA subcomponent. Such an anomalous behaviour for a “low K_a cluster” confirms, at posteriori, that the “non- degenerate” AA transitions are located in the low frequency range of the

“classical” triplet structures, since only the (AE & EA) sub components can be affected by this anomaly.

Figure 9 presents a portion of the ν_8 band in the 872 cm^{-1} spectral range. The agreement between observed and calculated spectra is generally satisfactory, except for the transitions involving the EE components of the $[10\ 2\ 8]$ level of the bright $\nu_8=1$ and the $[10\ 1\ 10]$ level of the 14^227^2 dark state, which are affected by a local C-type resonance. This is one example where the computation is not fully satisfactory.

Figure 10 shows the central part of the Q branch of the ν_{21} band. As compared to our previous investigation of the same band (see Fig. 5 of Ref. [30]) significant progress is achieved. Indeed, the previous Q branch investigation was restricted to K_a values with $K_a \leq 15$ instead of $K_a \leq 18$ in the present case.

c) Validation with the existing cross sections and “JPL pseudo lines”:

For this validation, we computed “artificial” low resolution cross sections at 296K and at 204K using our line list for the ν_8 and ν_{21} bands of propane. These simulations, here after identified as “ThisWork_Cross-296K” and “ThisWork_Cross-204K” were generated for a propane sample diluted in one atmosphere (Pressure=1013 hPa) of nitrogen, (line width of $\sim 0.1\text{ cm}^{-1}$) and for this calculation we used a Lorentzian line shape at the temperature of calculation in order to simulate approximatively the experimental conditions of the PNNL spectra.. Similarly the “JPL_Cross_204K” low resolution cross sections were generated using the JPL 296K pseudo line list and the pseudo “lower state energy” provided by the authors and the partition function given in Table B1 of Ref. [26]. Finally for “Wong_Cross_204K”, we degraded at the PNNL resolution the experimental cross sections from Wong et al. [28]. All these cross sections are plotted in Figure 11.

The upper trace of this figure is devoted to $T=296\text{K}$. On average, as expected, “This_Work_Cross_296K” are weaker than the PNNL values by a factor of ≈ 2.76033 , which is the $Z_{\text{vib}}(296\text{K})$ vibrational partition function at 296K (see Table 12) . In the central part of the ν_{21} band, three Q branch peaks are observable on the PNNL cross sections instead of one, at 921.8 cm^{-1} , in our model.

The bottom part of Fig. 11 compares computed cross sections at 204K. The Q branch of the ν_{21} band at 921 cm^{-1} looks prominent on the three plots, while the additional PNNL 923.5 and 924.9 cm^{-1} peaks which have almost disappeared at 204K are clearly due to hot bands. A similar behavior is observed on the Cassini CIRS spectra of the Titan atmosphere

(see Fig. 5 of Ref. 2]). We notice that at 204K the JPL [26] and Wong's [28] data are in perfect agreement, while, as expected, our cross sections are globally weaker. More precisely, the integrated band intensities in the 830-970 cm^{-1} spectral region are $^{\text{JPL}}S_{204\text{K}}=2.70$, $^{\text{Wong}}S_{204\text{K}}=2.60$, and $^{\text{ThisWork}}S_{204\text{K}}=1.63$ (in $10^{-19} \text{ cm}^{-1}/(\text{molecule.cm}^{-2})$ units). This leads to an average band intensity ratio $R(\text{JPL}/\text{This-Work})$ or $R(\text{Wong}/\text{This-Work})$ of $R \sim 1.618(\pm 0.034)$ and this is quite close to the value of the vibrational partition function at 204K ($Z_{\text{vib}}(204\text{K})=1.645645$), which is satisfactory.

It is then clear that the hot bands contribution must be accounted for in order to model properly the 296K signature at 11 μm . A first priority should concern the hot bands involving the ν_{14} and ν_{27} modes which contribute for 36% and 27% respectively relative to their cold band counterpart to the total band intensity.

Conclusion

The first high resolution investigation of the ν_8 band (A_1 , C-C stretch) located at 870.348 cm^{-1} , together with an extended analysis of the ν_{21} band (A_4 , CH_3 rock, at 921.382 cm^{-1}) of propane, (C_3H_8), are presented. For both bands, the overall set of transitions is affected by torsional splittings, leading to the identification of AA, EE and AE and EA sub components. A Hamiltonian model was set up for the computation of line positions taking into account these torsional splittings. More precisely an effective "vibration – torsion-rotation" Hamiltonian model was built which accounts both for anharmonic and Coriolis resonances coupling the 21^1 and 8^1 states with nearby highly excited states involving the two types of internal rotations of the methyl groups. In parallel, a line intensity code was set up for the computation of line intensities helping in the unambiguous assignment of the torsional components. The final result is a linelist of positions and intensities of the ν_8 and ν_{21} bands which could be used for the detection of propane in the Earth and outer planets atmospheres.

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Table List

Table 1 : Character table for the G_{36} inversion permutation group of propane.

G_{36}	E	$(123) \times (456)$	$(14) \times (26) \times (35) \times (C1C2)^*$	$(123) \times (465)$	(132)	$(142635) \times (78) \times (C1C2)^*$	$(14) \times (25) \times (36) \times (78) \times (C1C2)$	$(142536) \times (C1C2) \times (78)$	$(23) \times (56) \times (78)^*$		
A_1	1	1	1	1	1	1	1	1	1	T_b	
A_2	1	1	1	1	1	1	-1	-1	-1	T_c	J_a
A_3	1	1	-1	1	1	-1	1	1	1		J_b
A_4	1	1	-1	1	1	-1	-1	-1	-1	T_a	J_c
E_1	2	2	2	-1	-1	-1	0	0	0		
E_2	2	2	-2	-1	-1	1	0	0	0		
E_3	2	-1	0	2	-1	0	2	-1	0		
E_4	2	-1	0	2	-1	0	-2	1	0		
G	4	-2	0	-2	1	0	0	0	0		

Caption: The permutation operations involve the eight hydrogen nuclei (identified by numbers 1 to 8 (see Fig.2) and the carbon nuclei (C1 and C2) in the methyl groups. The * sign is for the inversion. The last two columns are for the a, b and c molecular fixed components of the translational (T_a) and rotational (J_a) operators.

Table 2 :

Symmetry species of the torsional wavefunctions (AA, AE, EA and EE) of the $[J K_a K_c]$ rotational energy levels in the ground vibrational state, of the 27 vibrational modes and of the E^+ , E^- , O^+ and O^- Wang's type wavefunctions.

G_{36}		Ground state torsional wavefunctions $ Tors\rangle$	Vibration	Rotation	Wang's type wavefunctions	
Γ		$(\sigma', \sigma)^*$		$K_a K_c$	J even	J odd
A_1	AA	$(0, 0)$	$\nu_1-\nu_9$	ee	E^+	E^-
A_2			$\nu_{22}-\nu_{27}$	eo	E^-	E^+
A_3			$\nu_{10}-\nu_{14}$	oo	O^+	O^-
A_4			$\nu_{15}-\nu_{21}$	oe	O^-	O^+
E_1	AE	$(1, -1), (-1, 1)$				
E_2						
E_3	EA	$(1, 1), (-1, -1)$				
E_4						
G	EE	$(1, 0), (-1, 0), (0, 1), (0, -1)$				

$*(\sigma_1, \sigma_2)$: torsional phase factor modulo 3, as defined in the text.

Table 3

Symmetry of the rotational energy levels and Wang’s type wavefunctions in G_{36} . Associated g_{spin} nuclear statistical weights are given.

Torsional states	Γ	Rotational	J even	J odd	g_{Spin}
AA $(\sigma_1, \sigma_2)=(0,0)$	A_1	ee	E+	E-	36
	A_2	eo	E-	E+	28
	A_3	oo	O+	O-	36
	A_4	oe	O-	O+	28
AE $(\sigma_1, \sigma_2)=(1,2)$ etc	E_1	ee & eo	E+ & E-	E+ & E-	16
	E_2	oo & oe	O+ & O-	O+ & O-	16
EA $(\sigma_1, \sigma_2)=(1,1)$ etc	E_3	ee & oo	E+ & O+	E- & O-	20
	E_4	eo & oe	E- & O-	E+ & O+	12
EE $(\sigma_1, \sigma_2)=(1,0)$ etc	G	All	all	all	64

Table 4

Nuclear weights associated to the torsional subcomponents for a $[J' K'_a K'_c] - [J K_a K_c]$ vibration rotation transition

(a) Low K_a values ("non degenerate" K_c) and clustered AE and EA subcomponents.

	$K_a K_c =$	$g_{\text{Nuclear}}^{\$}$			
		ee	eo	oe	oo
AA		36	28	28	36
EE		64	64	64	64
(AE & EA) [#]		36	28	28	36

(b) High or medium K_a values ("degenerate" K_c) and non clustered AE and EA

	$K_a K_c =$				$g_{\text{Nuclear}}^{\$}$
	(ee & eo) [#]	(eo & ee) [#]	(oe & oo) [#]	(oo & oe) [#]	
AA	(ee & eo) [#]	(eo & ee) [#]	(oe & oo) [#]	(oo & oe) [#]	64
EA	(ee & eo) [#]	(eo & ee) [#]	(oe & oo) [#]	(oo & oe) [#]	32
AE	ee	eo	oe	oo	16
EE	ee	eo	oe	oo	64

^{\$} associated nuclear weight in the ground vibrational state,

[#] clustered energy levels

Table 5: Results of the analysis and of the energy levels calculations

Results of the analysis

	v_8	v_{21}
Number of lines	6047	5054
Number of levels	1858 (v_8 bright) 6 ($2v_{14}+2v_{27}$ dark)	2244 (v_{21} bright) 7 (v_9+2v_{27} dark)
	AA: 497 EE: 745 AE [#] : 207 EA [#] : 415	AA: 584 EE: 781 AE [#] : 412 EA [#] : 474
Maximum J	43	44
Maximum K _a	17	16

[#] For low K_a values, the given EA or AE torsional labelling corresponds actually to clustered (EA & EA) levels (see text).

Statistical Analysis of the Results of the Energy Levels Calculations

Computation:	v_8	v_{21}
Total number of levels:	1864	2251
$0 \leq \delta \leq 0.002$	49.2%	36.7%
$0.002 \leq \delta \leq 0.004$	22.7%	30.7%
$0.004 \leq \delta \leq 0.020$	27.7%	31.0%
$0.020 \leq \delta \leq 0.050$	0.4%	0.5%
$0.050 \leq \delta \leq 0.090$		0.2%
Standard deviation (in 10^{-3} cm^{-1})	4.25	6.01

$$\delta = |E_{\text{obs}} - E_{\text{calc}}| \text{ in cm}^{-1}$$

Table 6

Hamiltonian matrices

v_8 calculation: $\{8^1, 14^2 27^2\}$ interacting states

	8^1	$14^2 27^2$
8^1	$H_{8,8}$	$H_{8,14142727}$
$14^2 27^2$	c.c	$H_{14142727, 14142727}$

v_{21} calculation: $\{21^1, 14^1 27^3, 9^1 27^2\}$ interacting states

	21^1	$14^1 27^3$	$9^1 27^2$
21^1	$H_{21,21}$	$H_{21,14272727}$	$H_{21,92727}$
$14^1 27^3$	c.c	$H_{14272727, 14272727}$	
$9^1 27^2$	c.c		$H_{92727, 292727}$

Caption: C.C stands for Complex Conjugate

Table 7

Symmetry- allowed Watson's type, anharmonic, and Coriolis type operators in the v - diagonal or $v' \Leftrightarrow v$ off diagonal blocks, according to the AA, AE, EA and EE torsional substates.

(a) Vibrational diagonal terms:

AA (σ_1, σ_2)=(0,0)	AE (σ_1, σ_2)=(1,-1)	EA (σ_1, σ_2)=(1,1)	EE (σ_1, σ_2)=(1,0)
H_{vv}^W	$H_{vv}^W + \text{CorA}_{vv}$	$H_{vv}^W + \text{CorB}_{vv}$	$H_{vv}^W + \text{CorA}_{vv} + \dots$ $\dots + \text{CorB}_{vv} + \text{CorC}_{vv}$

(b) Off diagonal vibrational terms :

$14^1 27^3$ $\Leftrightarrow 21^1$ or $14^2 27^2$ $\Leftrightarrow 8^1$	$\text{Anh}_{v'v}$	$\text{Anh}_{v'v} + \text{CorA}_{v'v}$	$\text{Anh}_{v'v} + \text{CorB}_{v'v}$	$\text{Anh}_{v'v} + \text{CorA}_{v'v} + \dots$ $\text{CorB}_{v'v} + \text{CorC}_{v'v}$
$9^1 27^2$ $\Leftrightarrow 21^1$	$\text{CorC}_{v'v}$	$\text{CorC}_{v'v} + \text{CorB}_{v'v}$	$\text{CorC}_{v'v} + \text{CorA}_{v'v}$	$\text{Anh}_{v'v} + \text{CorA}_{v'v} + \dots$ $\dots + \text{CorB}_{v'v} + \text{CorC}_{v'v}$

H_{vv}^W : Watson's type rotational operator

$\text{Anh}_{v'v}$: Anharmonic operator

$\text{CorA}_{v'v}$, $\text{CorB}_{v'v}$, $\text{CorC}_{v'v}$: A-type, B-type and C-type Coriolis operators (see Table 8).

The torsional dependence of these operators is given in Table 9.

Table 8

Expansion of the Watson's type rotational operator (I^r representation and A-type reduction), of the anharmonic ($Anh_{v'v}$) and of the A-type, B-type and C-type Coriolis ($CorA_{v'v}$, $CorB_{v'v}$, and $CorC_{v'v}$) operators.

$$\begin{aligned}
 H_v^W = & E_v + \left[A^v - \frac{1}{2}(B^v + C^v) \right] J_z^2 + \frac{1}{2}(B^v + C^v) J^2 + \frac{1}{2}(B^v - C^v) J_{xy}^2 \\
 & - \Delta_K^v J_z^4 - \Delta_{JK}^v J_z^2 J^2 - \Delta_J^v (J^2)^2 - \delta_K^v \{J_z^2, J_{xy}^2\} - 2\delta_J^v J_{xy}^2 J^2 \\
 & + H_K^v J_z^6 + H_{KJ}^v J_z^4 J^2 + H_{JK}^v J_z^2 (J^2)^2 + H_J^v (J^2)^3 \\
 & + h_K^v \{J_z^4, J_{xy}^2\} + h_{KJ}^v \{J_z^2, J_{xy}^2\} J^2 + 2h_J^v J_{xy}^2 (J^2)^2 + \dots \\
 Anh_{v'v} = & {}^0Anh + {}^1Anh J^2 + {}^2Anh \times J_z^2 + {}^3Anh \times J_{xy}^2 + {}^4Anh \times (J_+^4 + J_-^4) \\
 CorA_{v'v} = & {}^1CorA_{v'v} J_z + {}^2CorA_{v'v} \{iJ_y, J_x\} + {}^3CorA_{v'v} J^2 J_z + {}^4CorA_{v'v} J_z^3 \\
 CorB_{v'v} = & {}^1CorB_{v'v} J_x + {}^2CorB_{v'v} \{iJ_y, J_z\} + {}^3CorB_{v'v} J^2 J_x + {}^4CorB_{v'v} \{J_x, J_z^2\} \\
 CorC_{v'v} = & {}^1CorC_{v'v} iJ_y + {}^2CorC_{v'v} \{J_x, J_z\} + {}^3CorC_{v'v} J^2 iJ_y + {}^4CorC_{v'v} \{iJ_y, J_z^2\} + {}^5CorC_{v'v} (J_-^3 - J_+^3) \\
 \text{with } \{A, B\} = & AB + BA \quad \text{and } J_{xy}^2 = J_x^2 - J_y^2.
 \end{aligned}$$

Note that several of these parameters are presumed to be dependent on the considered torsional substate (see Table 9). However, for clarity, the (σ_1, σ_2) superscripts are written explicitly only when necessary.

Table 9

a) Sinusoidal expansion of the parameters involved in the Watson's type or anharmonic rotational Hamiltonians

$$\begin{aligned}
 E_v^{\sigma_1, \sigma_2} &= E_v^0 + \text{Tor}_0^v \times S_0^{\sigma_1, \sigma_2}(K_{\text{avr}}) + \sum_{q>0} \text{Tor}_q^v \times S_q^{\sigma_1, \sigma_2}(K_{\text{avr}}) \\
 \frac{1}{2}(B^v + C^v)^{\sigma_1, \sigma_2} &= \frac{1}{2}(B_0^v + C_0^v) + \sum_{q>0} BC_q^v \times S_q^{\sigma_1, \sigma_2}(K_{\text{avr}}) \\
 \frac{1}{2}(B^v - C^v)^{\sigma_1, \sigma_2} &= \frac{1}{2}(B_0^v - C_0^v) + 2 \sum_{q>0} bc_q^v \times S_q^{\sigma_1, \sigma_2}(K_{\text{avr}}) \\
 (A^v - (B^v + C^v)/2)^{\sigma_1, \sigma_2} &= (A_0^v - (B_0^v + C_0^v)/2) + \sum_{q>0} Abc_q^v \times S_q^{\sigma_1, \sigma_2}(K_{\text{avr}}) \\
 {}^0\text{Anh}_{v'v}^{\sigma_1, \sigma_2} &= {}^0\text{Anh}_{v'v}^0 + \sum_{q>0} \text{anh}_{v'v}^q \times S_q^{\sigma_1, \sigma_2}(K_{\text{avr}})
 \end{aligned}$$

Where the $S_q^{\sigma_1, \sigma_2}(K_{\text{avg}})$ are the sinusoidal terms and $K_{\text{avg}} = (K + K')/2$ is the average value of the K rotation quantum number in the $\langle JK\gamma | S_q^{\sigma_1, \sigma_2} | JK'\gamma' \rangle$ matrix element.

b) The $S_q^{\sigma_1, \sigma_2}(K_{\text{avg}})$ sinusoidal expansion

	AA	EE	EA	AE
$(\sigma_1, \sigma_2) =$	(0,0)	(1,0)	(1,1)	(1,-1)
$q=0$	0	1	2	2
$q=1$	$\cos(2\chi)$	$\frac{1}{4}\cos(2\chi) + \sqrt{\frac{3}{16}}\sin(2\chi)$	$-\frac{1}{2}\cos(2\chi) + \sqrt{\frac{3}{4}}\sin(2\chi)$	$-\frac{1}{2}\cos(2\chi)$
$q=2$	$\cos(4\chi)$	$\frac{1}{4}\cos(4\chi) - \sqrt{\frac{3}{16}}\sin(4\chi)$	$-\frac{1}{2}\cos(4\chi) - \sqrt{\frac{3}{4}}\sin(4\chi)$	$-\frac{1}{2}\cos(4\chi)$
$q=3$	$\cos(6\chi)$	$\cos(6\chi)$	$\cos(6\chi)$	$\cos(6\chi)$
$q=4$	$\cos(4\chi)$	$+\frac{1}{2}\cos(4\chi) + \sqrt{\frac{3}{4}}\sin(4\chi)$	$\cos(4\chi)$	$-\frac{1}{2}\cos(4\chi) - \sqrt{\frac{3}{4}}\sin(4\chi)$

With $\chi = \pi \rho K_{\text{avg}}/3$

Table 10

List of the Hamiltonian parameters determined during the energy level computations for the $\{8^1, 14^227^2\}$ interacting states of propane.

Table 10, Part A: 8^1 or 14^227^2 vibrational -diagonal operators:

(a) Watson’s type « torsion free » parameters

	$0^{(S)}$	8^1	14^227^2
E_V		870.39570(160)	872.5168(370)
Band centers ^(E)		870.3136(1)	872.4896(1)
A	0.9742562313	0.9742783(270)	1.141686(590)
B	0.2817271865	0.28019447(670)	0.279266(110)
C	0.2488055608	0.24757661(530)	0.2466803(970)
$\Delta_K \times 10^6$	5.324721011	4.4996(940)	509.75(850)
$\Delta_{KJ} \times 10^7$	-8.998168326	-10.355(410)	321.1(370)
$\Delta_J \times 10^7$	2.402258565	2.3561(340)	($\$$)
$\delta_K \times 10^7$	1.035202827	($\$$)	($\$$)
$\delta_J \times 10^8$	4.659136555	4.274(300)	20.13(600)
All higher order terms:	($\$$)	($\$$)	($\$$)

(b) Higher order Watson’s type rotational “torsion free” constants^(S)

$H_K \times 10^{10}$	1.147493844	$h_K \times 10^{12}$	-2.568443533	$L_K \times 10^{15}$	-2.625149429
$H_{KJ} \times 10^{11}$	-4.071816910	$h_{JK} \times 10^{12}$	1.377953277	$L_{KKJ} \times 10^{16}$	4.703253742
$H_{JK} \times 10^{13}$	5.193592962	$h_J \times 10^{13}$	1.197995448	$L_J \times 10^{19}$	-7.104915228
$H_J \times 10^{13}$	2.755239426				

(c) vibrational - diagonal “torsion free” Coriolis – type operators

8^1	$14^2 27^2$
${}^4\text{CorA}_{\text{v v}}^0$	${}^2\text{CorC}_{\text{v v}}^0$
$3.492(590) \times 10^{-6}$	$-1.154(160) \times 10^{-2}$

(d) q –type torsional dependence of the Watson-type rotational constants

	8^1	$14^2 27^2$
Tor_0^{v}	$0.0^{(\#)}$	$1.3522(250)$
$\text{Tor}_1^{\text{v}} \times 10^2$	$-0.505(120)$	
Tor_4^{v}		$-0.1042(110)$
$\text{Abc}_1^{\text{v}} \times 10^4$	$-1.911(140)$	
$\text{BC}_1^{\text{v}} \times 10^3$	$0.01776(340)$	$-1.382(130)$
$\text{bc}_1^{\text{v}} \times 10^5$	$1.053(250)$	

Table 10, Part B: vibrational off-diagonal operators:

(e) Torsion free $14^2 27^2 \leftrightarrow 8^1$ Off diagonal operators

Anharmonic		Coriolis	
$^0 \text{Anh}_{v'v}^0$	0.42609(830)	$^1 \text{CorA}_{v'v}$	$-1.736(120) \times 10^{-2}$
$^1 \text{Anh}_{v'v}^0$	$-1.972(130) \times 10^{-4}$	$^1 \text{CorB}_{v'v}$	$-7.848(460) \times 10^{-3}$
$^4 \text{Anh}_{v'v}^0$	$-2.167(620) \times 10^{-8}$	$^2 \text{CorB}_{v'v}$	$1.2059(750) \times 10^{-3}$
		$^4 \text{CorB}_{v'v}$	$-6.803(720) \times 10^{-5}$
		$^2 \text{CorC}_{v'v}$	$-1.2973(820) \times 10^{-3}$

(f) q-type torsional dependence of $14^2 27^2 \leftrightarrow 8^1$ anharmonic off diagonal operators

	Anharmonic	
$14^2 27^2 \leftrightarrow 8^1$	$\text{anh}_{v'v}^3$	$-2.401(330) \times 10^{-2}$

^(s) Fixed to the ground state values (Drouin *et al.* [16])

^(#) By definition, definition, Tor_0^v is fixed to zero for the 8^1 vibrational state (v_8 is a “low amplitude” vibrational mode)

^(£) Computed position for the “J=0” energy level of the AA component of the “v” vibrational state. The results are in cm^{-1} and the quoted uncertainties are one standard deviation.

Table 11

List of the Hamiltonian parameters determined during the energy level computations for the $\{21^1, 14^127^3, 9^127^1\}$ interacting states of propane.

Table 11, Part A: 21^1 , 14^127^3 or 9^127^2 vibrational -diagonal operators:

(a) Watson's type « torsion free » parameters

	21^1	14^127^3	9^127^2
E_v	921.5042(170)	932.0429(380)	909.4694(180)
Band centers ^(£)	921.3756(400)	932.1715(400)	909.4694(180)
A	0.9825827(110)	0.973887(450)	1.050674(630)
B	0.28155148(998)	0.2814147(470)	0.2894370(610)
C	0.24840146(710)	0.2479347(180)	0.2390320(760)
$\Delta_K \times 10^6$	9.374(190)	(\\$)	383.79(210)
$\Delta_{KJ} \times 10^7$	-5.48(130)	(\\$)	(\\$)
$\Delta_J \times 10^7$	3.256(120)	(\\$)	(\\$)
$\delta_K \times 10^7$	(\\$)	(\\$)	(\\$)
$\delta_J \times 10^8$	2.137(710)	(\\$)	(\\$)
Higher order terms:	(\\$)	(\\$)	(\\$)

(b) q-type torsional dependence of the Watson-type rotational parameters

	21^1	14^127^3
Tor_0^v	0.0 ^(#)	0.3972(180)
$Abc_1^v \times 10^4$	-1.887(190)	
$BC_2^v \times 10^6$	-9.38(220)	

(c) “Torsion free” 21^1 diagonal A-type Coriolis – type operators

	21^1
$^1\text{CorA}_{vv}$	$6.633(930)\times 10^{-4}$

Table 11, Part B: $14^1 27^3 \Leftrightarrow 21^1$ or $9^1 27^2 \Leftrightarrow 21^1$ off diagonal operators

(a) “Torsion free” $14^1 27^3 \Leftrightarrow 21^1$ anharmonic and C-type $9^1 27^2 \Leftrightarrow 21^1$ off diagonal operators

$14^1 27^3 \Leftrightarrow 21^1$	Anharmonic	${}^0 \text{Anh}_{v'v}^0$	1.1529(780)
$9^1 27^2 \Leftrightarrow 21^1$	C-type Coriolis	${}^1 \text{CorC}_{v'v}$	$2.315(200) \times 10^{-2}$
		${}^2 \text{CorC}_{v'v}$	$2.129(260) \times 10^{-3}$
		${}^3 \text{CorC}_{v'v}$	$3.344(190) \times 10^{-5}$
		${}^4 \text{CorC}_{v'v}$	$7.80(120) \times 10^{-5}$
		${}^5 \text{CorC}_{v'v}$	$-2.733(720) \times 10^{-6}$

(b) q-type torsional dependence of the $9^1 27^2 \Leftrightarrow 21^1$ anharmonic off diagonal operator

$9^1 27^2 \Leftrightarrow 21^1$	${}^0 \text{anh}_{v'v}^4$	$1.827(360) \times 10^{-2}$
---------------------------------	---------------------------	-----------------------------

^(s) Fixed to the ground state values (Drouin *et al.* [16])

^(#) By definition, Tor_0^v is fixed to zero for the 21^1 vibrational state (v_{21} is a “low amplitude” vibrational mode). Torsional splittings were not accounted for in the $9^1 27^2$ dark state.

^(E) Computed position for the “J=0” energy level of the AA component of the “v” vibrational state.

The results are in cm^{-1} and the quoted uncertainties are one standard deviation.

Table 12
Partition function for propane

Temperature (K)	$Z_{\text{rot}}(T)$	$Z_{\text{vib}}(T)$	$Z_{\text{tot}}(T)$
75.	3.27410E+05	1.02296	3.34927E+05
100.	5.03968E+05	1.07474	5.41636E+05
142..	8.52718E+05	1.23641	1.05431E+06
150.	9.25793E+05	1.27754	1.18274E+06
225.	1.70119E+06	1.83681	3.12476E+06
273.15	2.27615E+06	2.40767	5.48022E+06
296.	2.56781E+06	2.76033	7.08799E+06
300.	2.62008E+06	2.82871	7.41146E+06

Table 13

(a) Results of the intensity computation at 142 K

Band	Number of lines	Band Intensity	Int _{Max}	Sigma Min	Sigma Max	J _{Max}	Ka _{Max}
ν_{21}	35098	0.141E-19	0.93E-22	881.79	957.74	66	32
$\nu_9+2\nu_{27}$	8657	0.163E-20	0.29E-22	855.26	952.90	60	17
$\nu_{14}+3\nu_{27}$	13574	0.200E-20	0.24E-22	886.76	955.27	63	22
		0.147E-19					
ν_8	55847	0.871E-19	0.48E-22	812.43	930.43	65	31
$2\nu_{14}+2\nu_{27}$	8531	0.137E-20	0.11E-22	816.31	925.35	61	27
		0.899E-19					
Total: ν_8 & ν_{21}	121707	0.233E-18					

(b) Results of the intensity computation at 296 K

Band	Number of lines	Band intensity	Int _{Max}	Sigma Min	Sigma Max	J _{Max}	K _{aMax}
ν_{21}	57409	0.623E-19	0.20E-22	856.44	963.64	74	40
$\nu_9+2\nu_{27}$	15424	0.120E-20	0.85E-23	817.32	967.02	74	21
$\nu_{14}+3\nu_{27}$	20482	0.118E-20	0.50E-23	857.92	962.85	74	24
		0.646E-19					
ν_8	90942	0.387E-19	0.11E-22	790.91	945.00	74	40
$2\nu_{14}+2\nu_{27}$	11752	0.620E-21	0.31E-23	807.54	930.94	74	28
		0.393E-19					
Total: $\nu_8 \& \nu_{21}$	195709	0.104E-18					

Caption:

Band intensity: in $\text{cm}^{-1}/(\text{molecule}.\text{cm}^{-2})$

Int_{Max}: in $\text{cm}^{-1}/(\text{molecule}.\text{cm}^{-2})$

Sigma Min and Sigma Max: in cm^{-1}

Figure 1

Overview of the ν_8 and ν_{21} bands of propane. Spectrum recorded with the high resolution FT spectrometer at SOLEIL (partial pressure of 14 Pa, temperature = 142 K and optical path length of 45.14 m). The distinctive shapes of the typical B-type (ν_8) and A-type bands (ν_{21}) are clearly visible. The experimental spectrum is compared to the calculation performed during this study.

Figure 2

Overall structure of propane [7]. The numbering of the nuclei correspond to the convention adopted in Table 1.

Figure 3 :

Range of “degenerate” (“ $K_c = d$ ”) and “non degenerate” (“ $K_c \neq d$ ”) energy levels of propane in the ground vibrational state, with a boundary limit of $\delta_{\text{limit}} = \sim 0.001 \text{ cm}^{-1}$ for the energy separation of the $[J, K_a, K_c = J - K_a]$ and $[J, K_a, K_c = J - K_a + 1]$ levels, see text).

Figure 4: Portion of the R branch of the ν_{21} band around 931.3 cm^{-1} .

CAPTION: For transitions involving low K_a values, three components (AA, EE, and AE&EA) are observed with the intensity pattern described in Table 4. The structure of the torsional substructure is significantly more complex for transitions involving high K_a values.

Figure 5 : Portion of the R branch of the ν_{21} band in the 926.88 cm^{-1} .

CAPTION: For the $[10, 5, K'_c] - [9, 5, K''_c = d]$ rotational transition six torsional subcomponents are observable since we are dealing with rather high K_a values ($K_a = 5$).

Figure 6 : Portion of the R branch of the ν_8 band of propane.

CAPTION: Most of the transitions are B- type transitions. However for intermediate K_a values (see Figure 3), the stars (*) indicate C-type transitions which are also observable for EE and AE subcomponents.

Figure 7 Portion of the P branch of the ν_{21} band around 913 cm^{-1} .

CAPTION: For transitions involving intermediate K_a values, forbidden transitions (with $\Delta K_a = \text{even}$, $\Delta K_c = \text{even}$ selection rules) marked by stars (*) are observable for EE and AE components.

Figure 8: Portion of the P branch of the ν_{21} band for transitions involving low K_a values.

CAPTION: Three components (AA, EE, and AE&EA) are observed with the intensity pattern described in Table 6. One of the very few exceptions is observed for the P and R transitions involving the [11 3 9] level of $\nu_{21} = 1$ for which the AE and EA subcomponents are splitted by a local resonance.

Figure 9: Portion of the ν_8 band in the 872 cm^{-1} spectral range.

CAPTION: The quoted assignments are the upper energy levels for RQ -type transitions. A resonance is affecting the $[10, 2, 8]$ EE subcomponent of the 8^1 bright state which is perturbed by a local C-type Coriolis resonance involving the $[10, 1, 10]$ EE subcomponent of the $14^2 27^2$ dark state. This resonance could not be accounted for satisfactorily by the calculation, and at 871.962 cm^{-1} (resp. at 871.983 cm^{-1}) the line intensity is overestimated (resp. underestimated) by the calculation.

Figure 10 : Central part of the Q branch of the ν_{21} band. The K_a band head assignments are quoted.

Figure 11 : Comparison of experimental and simulated cross sections.

CAPTION: The upper and lower panels refer to temperatures $T = 296$ K and $T = 204$ K, respectively.

fig 1

287x201mm (300 x 300 DPI)

fig 2

198x135mm (96 x 96 DPI)

fig 3

279x215mm (150 x 150 DPI)

Fig 4

279x215mm (150 x 150 DPI)

fig 5

279x215mm (150 x 150 DPI)

Fig 6

279x215mm (150 x 150 DPI)

fig 7

279x215mm (150 x 150 DPI)

fig 8

279x215mm (150 x 150 DPI)

fig 9

279x215mm (150 x 150 DPI)

fig 10

279x215mm (150 x 150 DPI)

fig 11

279x215mm (150 x 150 DPI)